



# Complex Hydrides – A New Frontier for Future Energy Applications



## Mechanochemistry, Nanostructuring and Potential for Reversibility

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# New BES-funded research effort



- Ames Laboratory:
  - Vitalij Pecharsky, Oleksandr Dolotko, Haiqiao Zhang
  - Scott Chumbley, Ozan Ugurlu
  - Marek Pruski, Jerzy Wiench
  - Victor Lin, (Cedric) Po-Wen Chung
- Virginia Commonwealth University:
  - Purusottam Jena, Sa Li



# Approach



- Synthesis and processing:
  - Transformations of complex hydrides in solid state
  - Nanostructuring
    - Stochastic (mechanochemistry)
    - Controlled (micelle self assembly in non-polar organic solvents)
  - Solid state synthesis
  - High H-pressure mechanochemistry (near future)
- Characterization:
  - Diffraction and microscopy
  - Solid state NMR
  - PCI (PCT-PRO from HyEnergy LLC, near future)
- Theory and computation:
  - Super-cell band structure methodology
    - Density functional theory
    - Generalized gradient approximation
    - PAW potential
    - VASP code

# Mechanochemistry

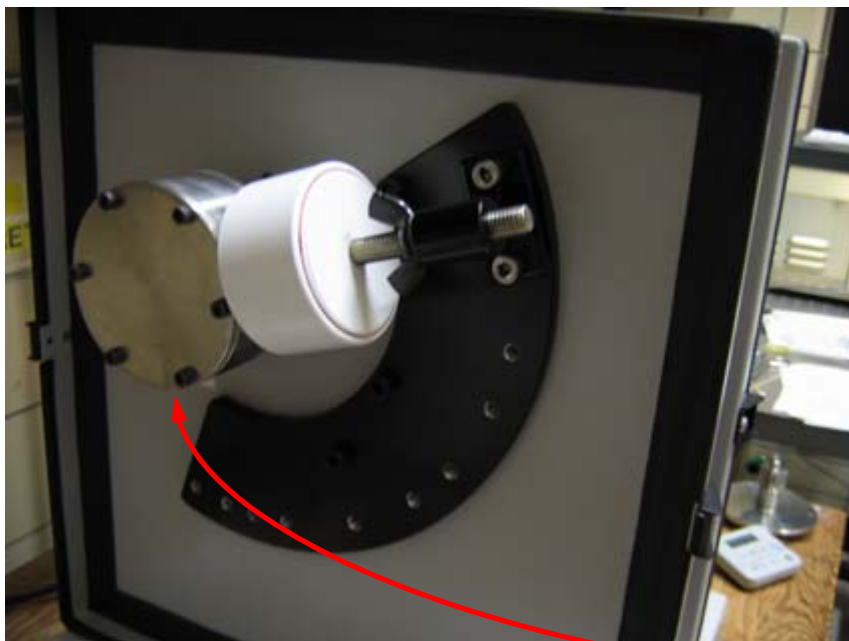


SPEX: high energy; control by balls-to-material mass ratio



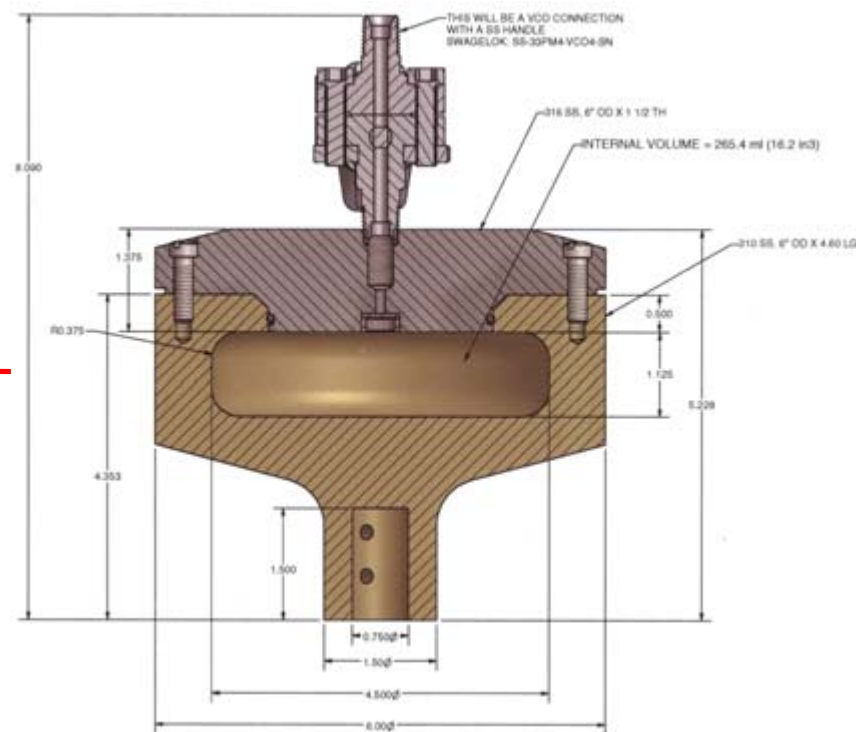
Magnetic: variable energy; control by rpm and positioning of the magnets

# High H-pressure mechanochemistry



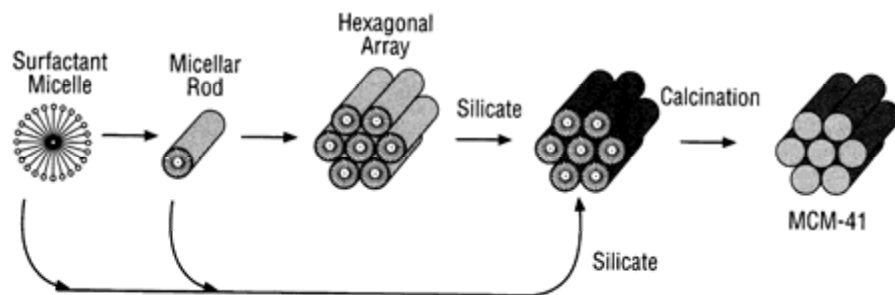
Design completed  
Manufacturing will be completed mid-June  
Readiness review and operational approval  
is expected by the end of June

Maximum H-pressure **300 bar**



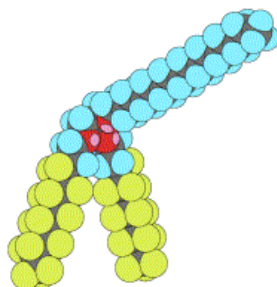
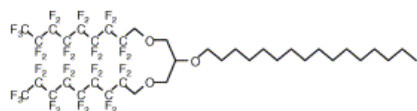
# Micelle self-assembly

- The conventional strategy of using surfactant micelles as structure-directing templates (e.g., for metal oxide synthesis) can only work in aqueous solutions.

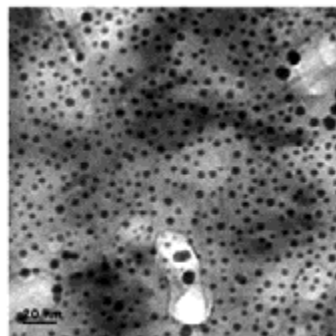


Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature*, **1992**, 359, 710.

- Utilizing fluorohydrocarbon molecules that can form micelles in nonpolar organic solvents will facilitate synthesis of nanostructured metal hydride materials.



Micelle Formation in dodecane



W. Huang , C. Jin , D. K. Derzon , T. A. Huber , J. A. Last , P. P. Provencio , A. S. Gopalan , M. Dugger, and D. Y. Sasaki. *J. Colloid Interface Sci.* **2004**, 272(2), 457.

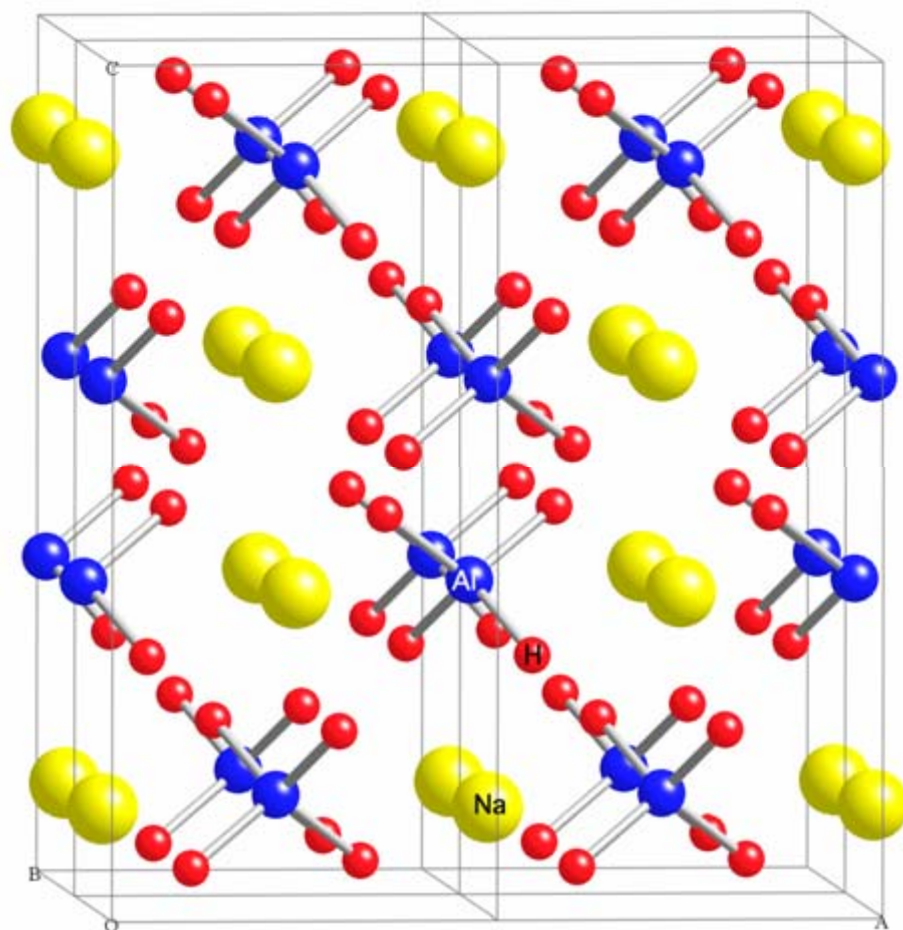
# Solid state NMR

- **Instruments:**
  - Chemagnetics Infinity and Varian NMR systems operated at 9.4 T and 14.1 T
  - Triple resonance probes capable of MAS at speeds up to 3M rpm
  - Variable temperature capabilities
- **Advanced solid state methods:**
  - High resolution techniques for solids: magic angle spinning (MAS), multiple quantum (MQ) MAS, homo- and hetero-nuclear decoupling
  - Multi-resonance, multi-dimensional experiments for studying the internuclear correlations
  - Nuclei:  $^1\text{H}$ ,  $^7\text{Li}$ ,  $^{11}\text{B}$ ,  $^{23}\text{Na}$ , and  $^{27}\text{Al}$
- **Arsenal used to:**
  - Identify the composition, local environment and structure of complex hydrides
  - Follow the mechanochemically and thermally induced transformations of these materials
  - Study the hydrogen dynamics and solid state hydrogenation-dehydrogenation processes

V.P. Balema, J.W. Wiench, K.W. Dennis, M. Pruski, V.K. Pecharsky, *J. Alloys Comp.* 329 (2001) 108-114  
J.W. Wiench, V.P. Balema, V.K. Pecharsky, M. Pruski, *J. Solid State Chem.* 177 (2004) 648-653



# Super-cell methodology



**$\text{NaAlH}_4$**

**$2 \times 2 \times 1$**

**96 atoms total**



# Why complex hydrides?

$\text{LaNi}_5\text{H}_{6.7}$  – 1.5 wt.%  $\text{H}_2$  1960's – 1990's

$\text{Mg}_2\text{NiH}_4$  – 3.6 wt.%  $\text{H}_2$  1970's – ...

$\text{MgH}_2$  – 7.6 wt.%  $\text{H}_2$

$\text{NaAlH}_4$  – 7.4 wt.%  $\text{H}_2$

$\text{LiNH}_2$  – 8.7 wt.%  $\text{H}_2$

$\text{LiAlH}_4$  – 10.5 wt.%  $\text{H}_2$

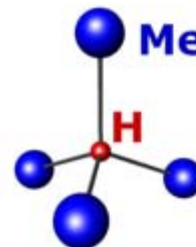
$\text{NaBH}_4$  – 10.5 wt.%  $\text{H}_2$

$\text{Li}_3\text{AlH}_6$  – 11.1 wt.%  $\text{H}_2$

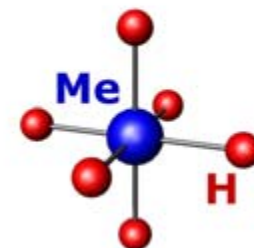
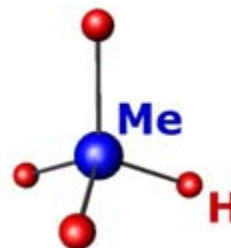
$\text{LiBH}_4$  – 18.2 wt.%  $\text{H}_2$

1997 – ...

Conventional metal-hydrides

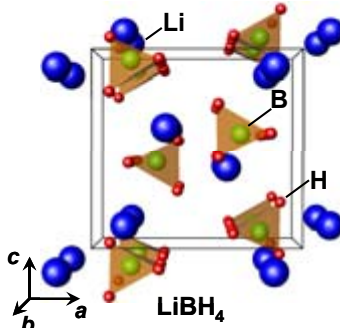
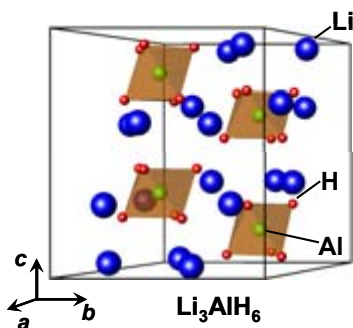
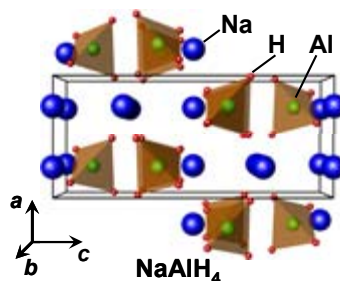
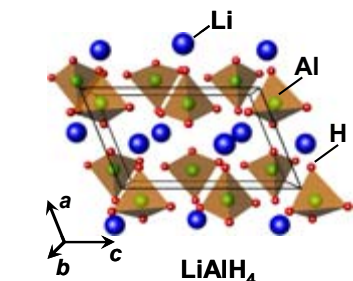


Complex metal-hydrides



Alanates (aluminumhydrides), amides & borohydrides

# Fundamental issues



- Covalent M-H bonds are strong
- “Destabilization” is required
- Multiple-stage hydrogenation and dehydrogenation reactions
- Tuning thermodynamics by chemical substitutions is far from trivial
- Long-range mass transport and detrimental kinetics

# Destabilization by doping

7.4 wt.% H total,  
 $\frac{3}{4}$  or 5.6 wt.% usable

9% of H-content  
Is irreversibly lost!



6.2 wt.% H total,  
 $\frac{3}{4}$  or 4.7 wt.% usable:  $\sim 16\%$  loss of reversible capacity

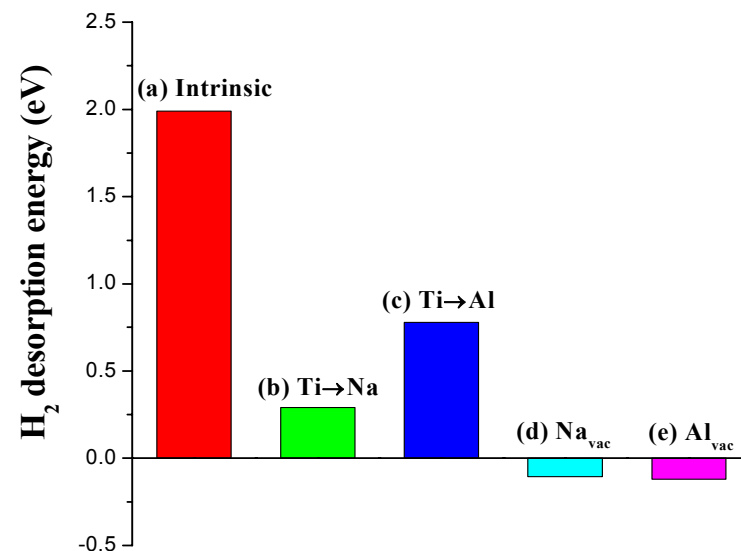
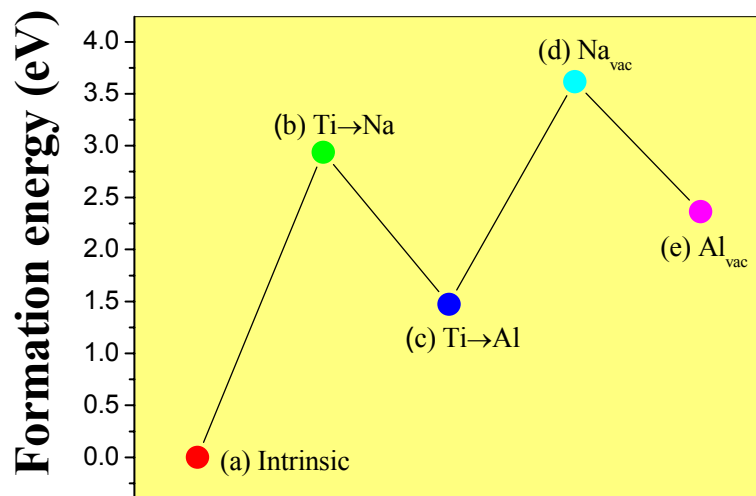
10.5 wt.% H total,  
 $\frac{3}{4}$  or 7.9 wt.% usable

9% of H-content  
Is irreversibly lost!

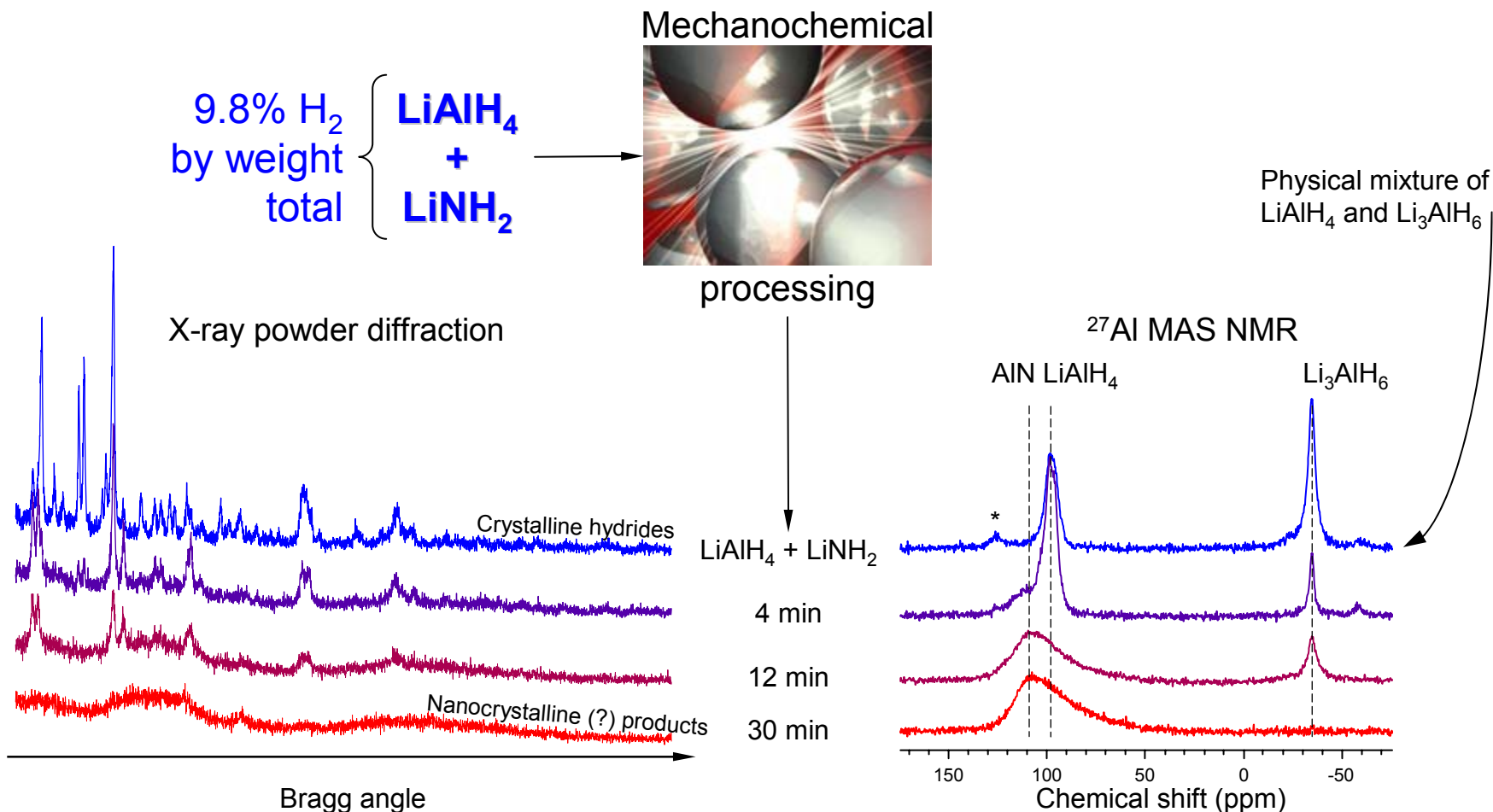


8.5 wt.% H total,  
 $\frac{3}{4}$  or 6.4 wt.% usable:  $\sim 19\%$  loss of reversible capacity

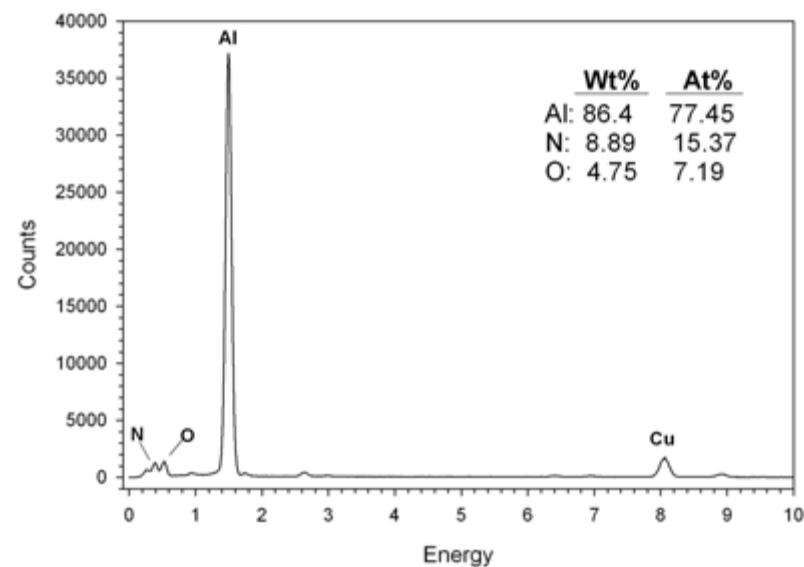
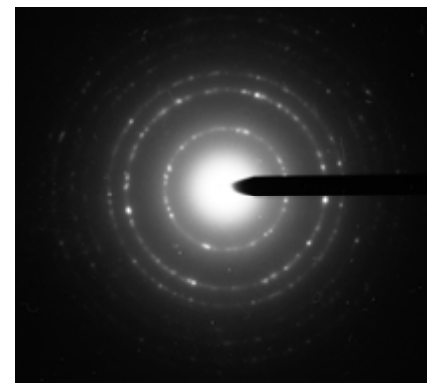
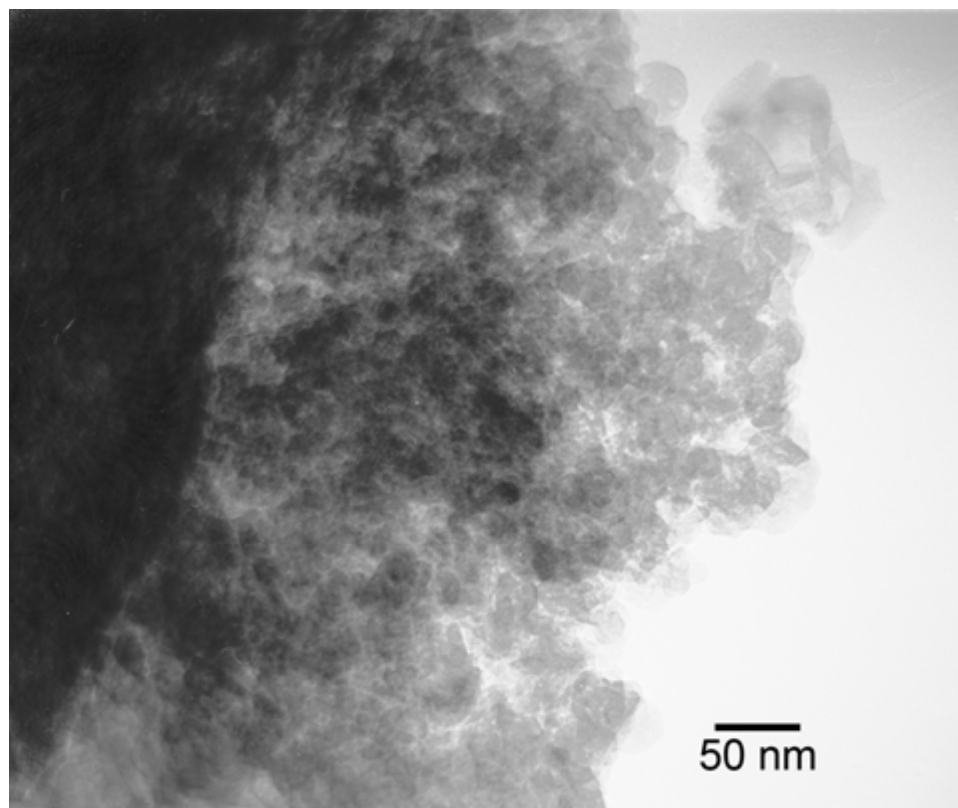
# Can Al-H bonds be destabilized without Ti-doping?



# Destabilization by synergy



# The products are nanocrystals

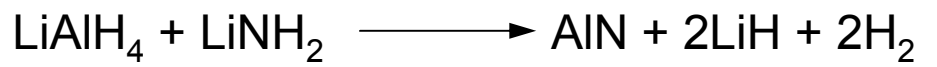




# Overall dehydrogenation reaction

Time of the ball milling, min	LiAlH <sub>4</sub>	LiNH <sub>2</sub>	Li <sub>3</sub> AlH <sub>6</sub>	AlN	LiH	Al
0 min	+	+	—	—	—	trace
4 min	↓	↓	+	+	+	—
12 min	↓	↓	↑	↑	+	—
30 min	—	—	—	+	+	—

30 min in a SPEX

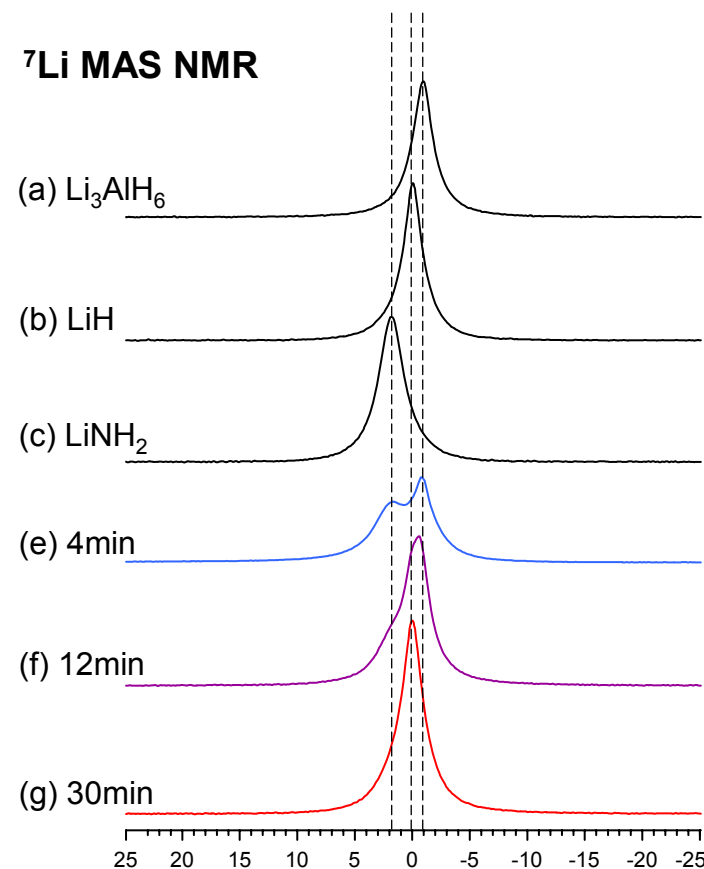


240 min in magnetic

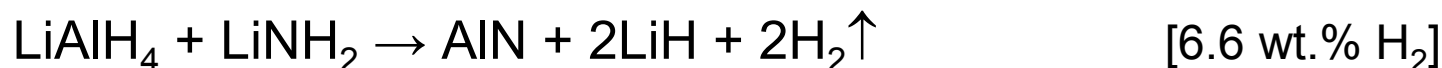
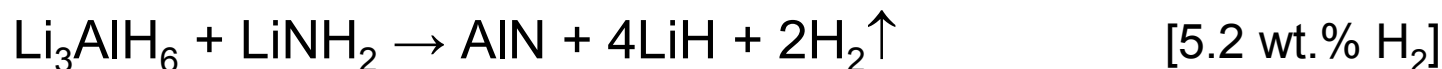
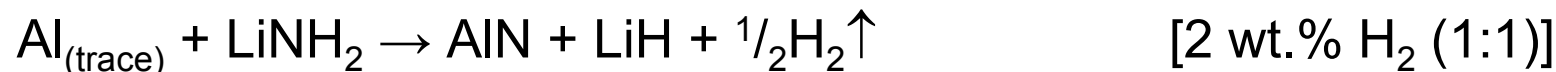
6.6 wt.% H<sub>2</sub>

Only 4.3 wt.% H<sub>2</sub> may be obtained mechanochemically from Ti-destabilized LiAlH<sub>4</sub> [Balema et al., Chem Comm. 1665 (2000)]

## <sup>7</sup>Li MAS NMR



# Possible mechanism



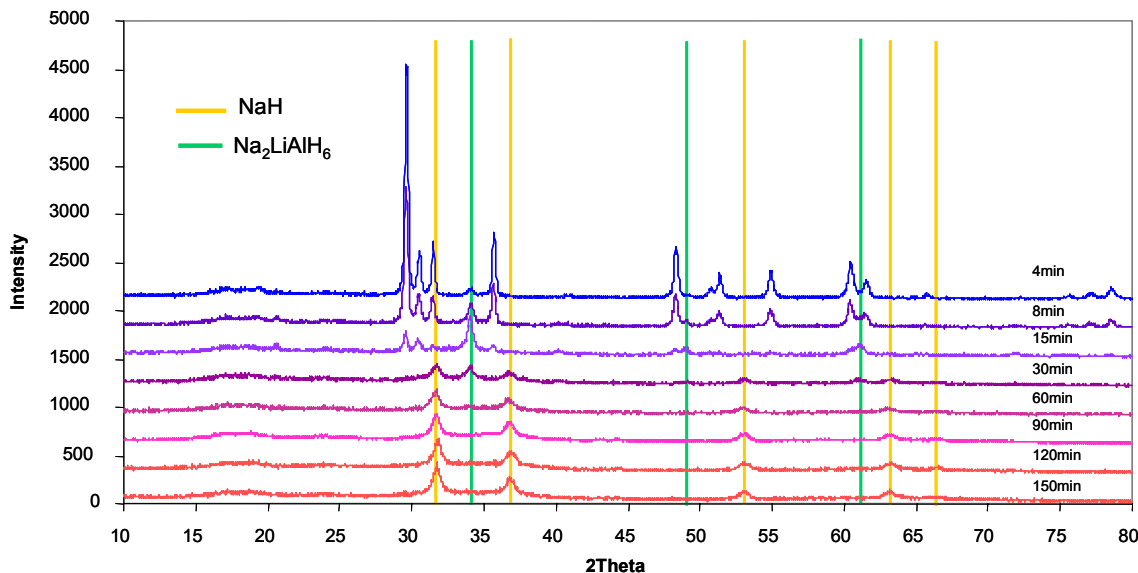
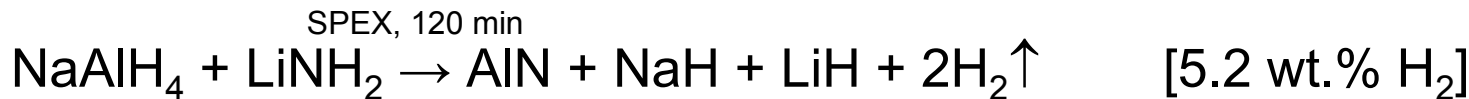
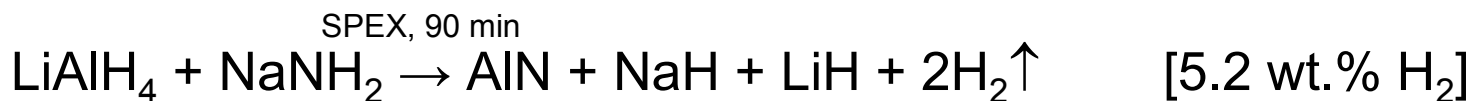
All of these reaction pathways have been verified experimentally

There is a competition between different reaction pathways

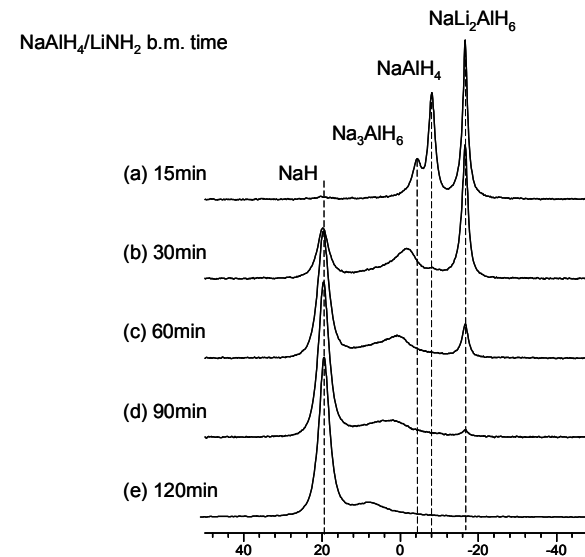
Other pathways are possible

Working with theorists in order to establish the most favorable energetics

# Mechanochemistry of related complex hydride systems

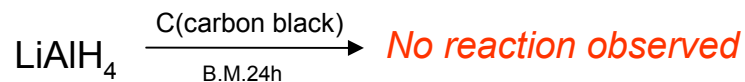
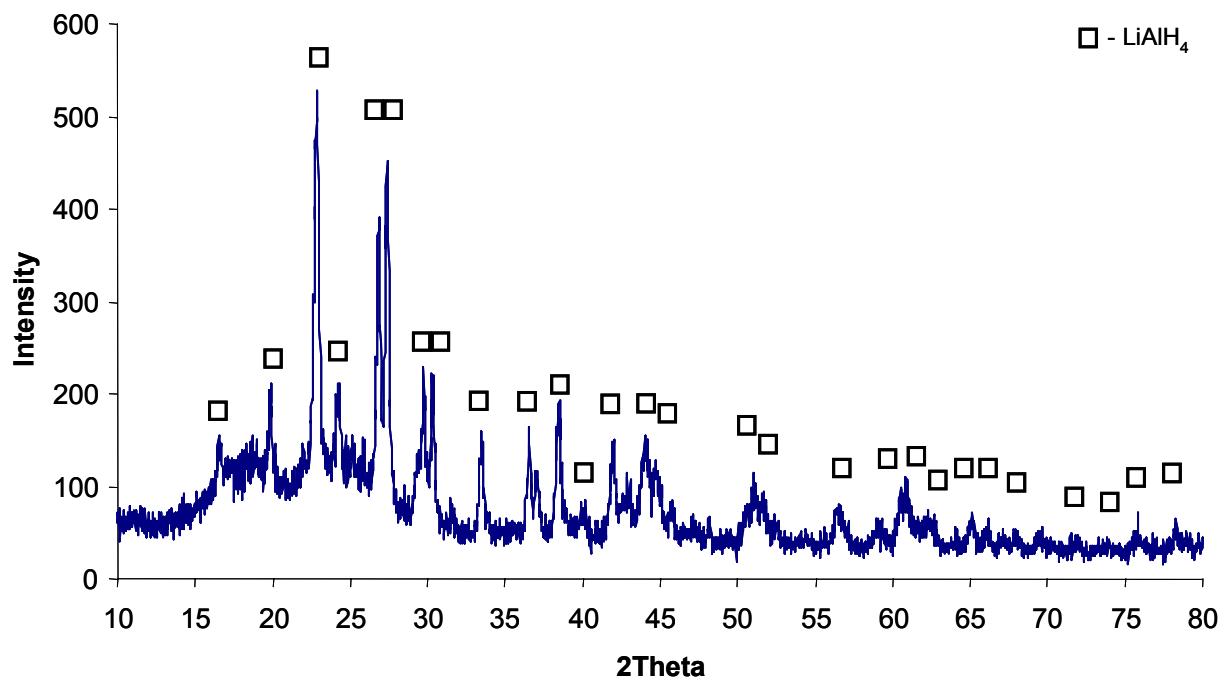


<sup>23</sup>Na MAS spectra



# Mechanochemistry of alanate-carbon systems

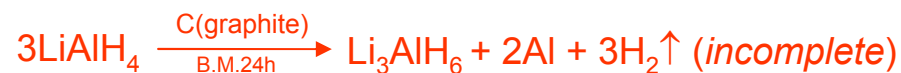
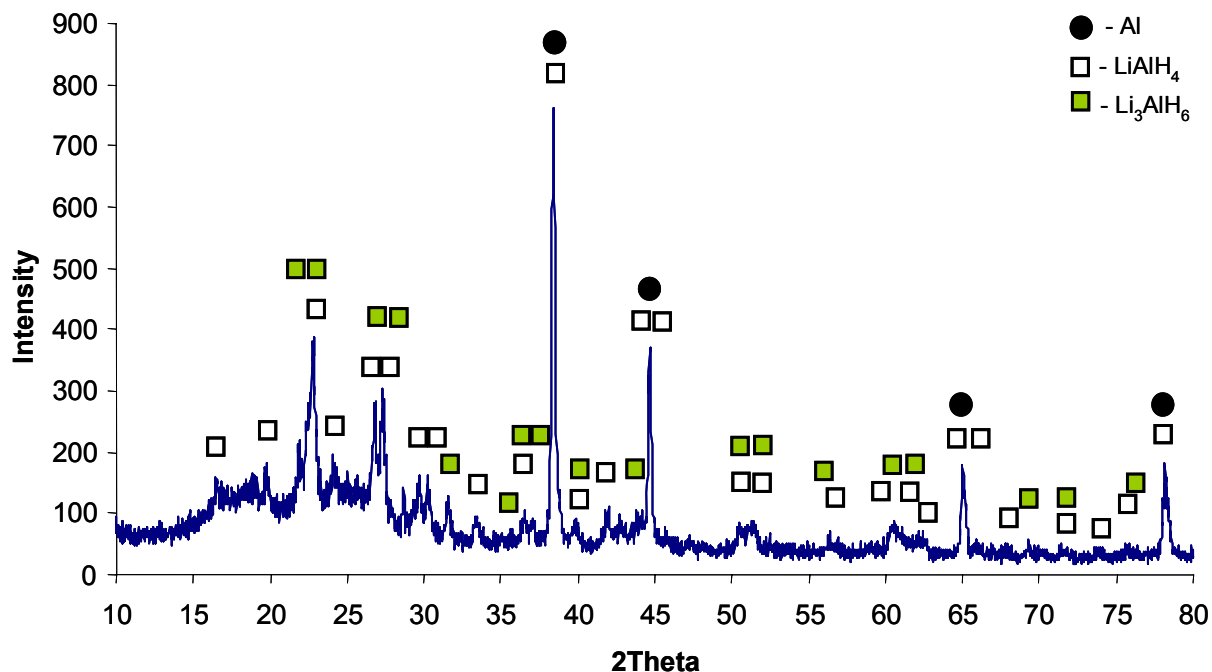
$\text{LiAlH}_4 + \text{C}(\text{carbon black}) (1:1)$  ball milling 24h



Covalent-only C-C bonds

# Mechanochemistry of alanate-carbon systems

LiAlH<sub>4</sub>+C(graphite) (1:1) ball milling 24h



Covalent plus  $\pi$  C-C bonds

Working with theorists to understand the role of C-C bonding in the activity of carbon



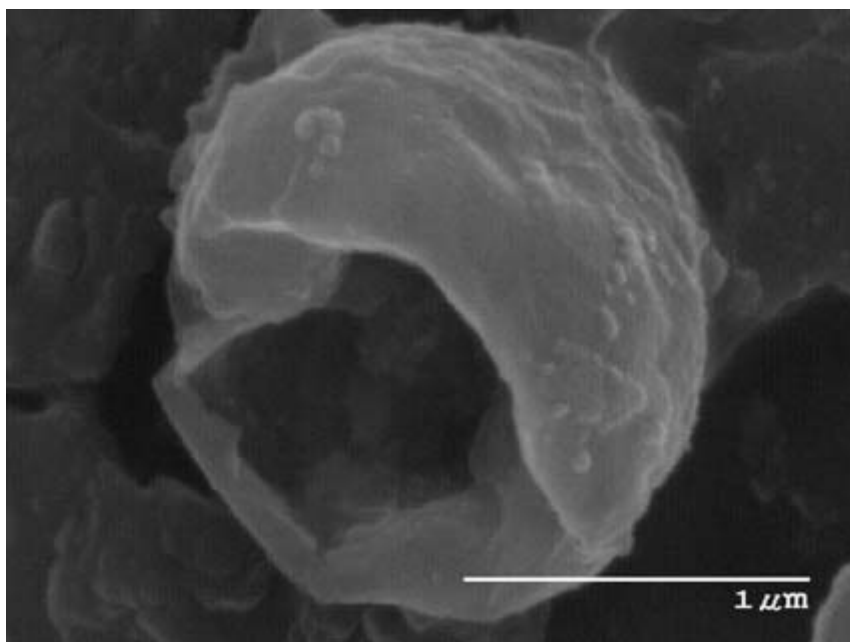
# Mechanochemical advantage

- Doping (e.g., with  $\text{TiHal}_3$ ) not needed
- Synergy between  $\text{LiAlH}_4$  and  $\text{LiNH}_2$
- Related systems exhibit similar effects
- Nearly **33% more** hydrogen released quickly and in a “single” step compared to  $\text{TiCl}_3$ -doped  $\text{LiAlH}_4$
- No heating, easy control of hydrogen release by controlling mechanical energy
- Hydrogen release/uptake is fundamentally reversible
- Nanocrystallinity = short diffusion paths
- Mechanochemically promoted rehydrogenation offers a possibility to maintain nanocrystallinity of a fully hydrided material

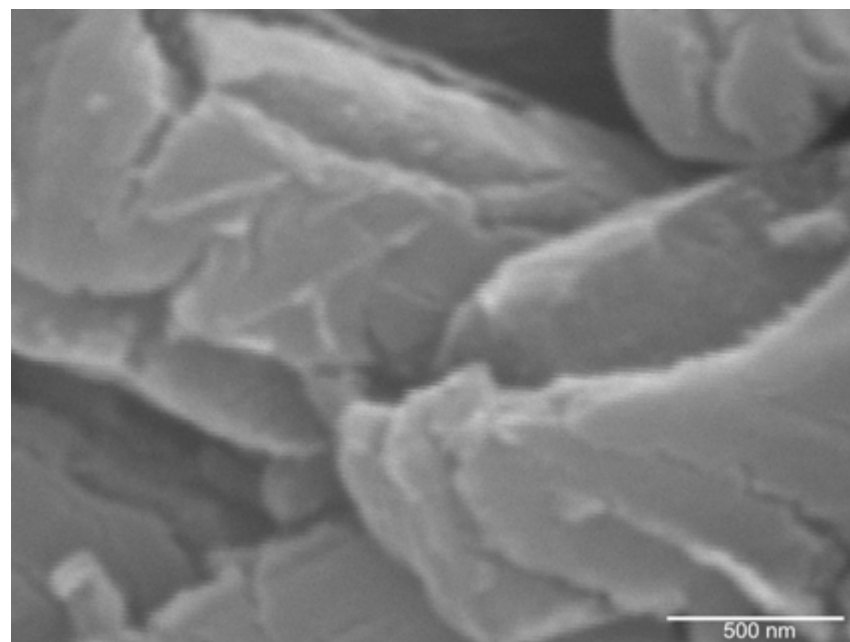


# Controlled nanostructuring

- Initial difficulties in synthesis of the needed fluorohydrocarbon molecules
- Demonstrated effect of fluorohydrocarbon molecules as structure-directing templates



Fluorohydrocarbon-templated



Without the fluorohydrocarbon template



# Future work



- In concert with theoretical predictions, explore mechanochemistry of novel mixed complex hydride systems
- In collaboration with theoretical and computation effort establish reaction mechanisms
- Thermodynamic and kinetic studies using (PCT PRO delivery is scheduled at the end of May, safety and readiness review is scheduled at the end of June)
- High H-pressure mechanochemical processing to establish reversibility of the most interesting systems